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Correlations Between the Ligand Electrochemical Parameter, $E_L(L)$ and the Hammett Substituent Parameter, σ

By

Hitoshi Masui and A.B.P. Lever*

in

Inorganic Chemistry

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York University
Department of Chemistry, 4700 Keele St., North York
Ontario, Canada M3J 1P3

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Cleveland, OH 44106

Contribution from the Dept. of Chemistry,
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Ontario, Canada, M3J 1P3.

Correlations Between the Ligand Electrochemical Parameter, $E_L(L)$ and the Hammett Substituent Parameter, σ .

By Hitoshi Masui and A. B. P. Lever.

Correlations of the electrochemical parameter, $E_L(L)$ with Hammett and Taft parameters, σ_p , σ_m , σ^+ and σ^* are presented and discussed. The correlations provide a means to extend the electrochemical parameter and the Hammett and Taft databases.

Recently, a ligand electrochemical parameter, $E_L(L)$, based upon the $\text{Ru}^{III}/\text{Ru}^{II}$ reduction potential as an electrochemical standard, was introduced¹⁻³ and developed.⁴⁻¹⁴ This parameter allows one to predict the metal-centred redox potential of a variety of complexes based on the additivity of the $E_L(L)$ parameters. The prediction is made using the linear relationship,

$$E_{(obs)} = S_M [\Sigma E_L(L_i)] + I_M \quad (1)$$

where the slope, S_M , and the intercept, I_M , are constant for all derivatives of a given metal undergoing a defined redox process; i.e. having a defined initial and final oxidation state, coordination number, stereochemistry, and spin state.

Hammett σ parameters have been shown to correlate with, inter alia, metal centered electrochemical potentials in a variety of substituted ligand complexes.¹⁵⁻³¹ It follows that, in these cases, Hammett parameters must also linearly correlate with $E_L(L)$ values, as briefly noted for substituted benzoquinonediimine species.^{3,32}

In this exploratory paper we consider possible relationships between Hammett or Taft parameters with $E_L(L)$ parameters. The question of whether it is better to use σ_p , σ_m , σ^+ or σ^* is discussed briefly. From a pragmatic point of view, correlation with σ_p or σ_m is preferred since there is a large database of these parameters for a wide variety of substituents. For example, σ_m and σ_p values for some 530 substituents are listed in Table I of ref. 33. However, when the substituent is closer to the metal and metal-substituent π interactions are possible, σ^* or σ^+ may be more appropriate.

It should be possible to use Hammett or Taft parameters to derive $E_L(L)$ values for a large variety of ligands not covered in ref. 1, thereby, greatly expanding the utility of the electrochemical parameter analysis. In particular the availability of Hammett parameters for a great number of organic functional groups should permit these $E_L(L)$ parameters to be used to derive redox potentials in a variety of organometallic species. Their availability should spur the synthesis of more exotic complexes by defining a potential range for their isolation. Further, electrochemically generated $E_L(L)$ values may then be used to obtain σ values for hitherto unreported substituents. This paper begins the exploration of such a correlation but is restricted to a single- rather than multi-parameter correlation.

The relationship between the $E_L(L)$ parameter and the σ parameter can be deduced from the mathematical definition of the $E_L(L)$ parameter (Eqn. 4b of Ref.¹), the Nernst equation³⁴ and the equations expressing the Hammett free-energy relationship.^{31,35,36} Thus, the $E_L(L)$ parameter of a substituted ligand, LX, (LH denotes a parent ligand substituted by X which may also generally represent a collection of substituents as in the case of poly-substituted ligands) is given by:³⁷

$$E_L(LX) = 2.303(RT/nF)\rho(L)_{Ru^{III}/II} \sum \sigma + E_L(LH) \quad (2)$$

Here, $\rho(L)_{Ru^{III}/II}$, the reaction parameter, characterizes the sensitivity of the Ru^{III/II} redox potential to substitution at L for the series, and $\sum \sigma$ is the sum of the Hammett or Taft parameters of the substituent(s) attached to L, and $E_L(LH)$ is the $E_L(L)$ parameter of the unsubstituted ligand. The remaining constants retain their usual meanings.^{1,33-36} The reaction parameter is the fitted parameter.

Based on previous literature,¹⁵⁻³¹ a correlation can be expected between $\sum \sigma$ and $E_L(L)$ for homologous series such as substituted pyridines R-Py, substituted bipyridines, 4-R,4'-R',5-R'',5'-R'''bpy, R, R',R''-phosphines, diketones (RCOCHR'COR''), and

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benzoquinonediimines, R-BQDI, for which a significant $E_L(L)$ database^{1,32} is available. In the pyridine and bipyridine series, it is reasonable to use the σ_p and σ_m parameters for substituents on the aromatic rings which are para or meta to the coordinating atoms; regression data are shown in Table 1. In the case of the phosphines and diketones, where the substituent is closer to the reaction centre, parameters such as σ^+ , σ^* or R ,^{33,39,40} which incorporate a resonance or π interaction may be more appropriate given the importance of these interactions in determining the ligand's $E_L(L)$ value.¹ In the case of the phosphines (including phosphites) there are too few available σ^+ parameter values to be very useful. A good correlation was observed with σ^* (Table 1) and fairly good correlations were also observed for σ_p and σ_m although they were statistically less well behaved than σ^* . Correlation with R was very poor. One may question whether σ^* values are truly additive when dealing with several substituents on the same atom (phosphorus) and a more detailed analysis of such an assumption is left for future analysis. An excellent correlation is observed for the diketone species with σ^+ , much better than with σ^* . Good correlations are also observed with both σ_p and σ_m , but the application of σ^+ is more appropriate in this case (Table 1).

While good linear correlations were obtained for all the homologous series studied (Table 1), one should note the narrow range of E_L parameters for each series (except perhaps the bipyridines) so that a good correlation while useful, is not so surprising or dramatic.

The $\rho_{RuIII/II}$ parameters do not vary greatly between these series and are largest for substituted benzoquinonediimines^{32,41} and phosphines, where electronic coupling to the metal centre is known to be very strong. Surprisingly, the reaction parameter for the pyridine series is twice that for the bipyridine series showing that substituent effects are transmitted much more readily to ruthenium in the pyridine series than in the bipyridine series. This may be due to a steric effect.

Of more profound value, a correlation with σ_p was also noted between a large number of neutral and anionic ligands which may be regarded as substituents of a hydrido $M(L')_nH$ species. Thus if the substituent is attached directly to the metal,

$$E_L(X^-) = 2.303(RT/nF)^\rho_{RuIII/II} \sum \sigma + E_L(H^-) \quad (3)$$

For example (Table 2), NH_3 and Cl^- ligands may replace the hydrido ligand on ruthenium just as NH_3^+ and Cl would replace the hydrogen of an organic molecule. Such analogies have been drawn

previously between organic and inorganic fragments.³⁸

The validity of Eqn. 3 may be tested by plotting the $E_L(L)$ data listed in Table 2 against σ_p as in Figure 1. Indeed, quite a good linear correlation is observed between the two parameters with the y-intercept gratifyingly close to the $E_L(H^-)$ value of the hydride ligand. As expected, the sensitivity of the Ru^{III/II} redox potential to direct substitution, as indicated by $\rho_{Ru^{III/II}}$, is much greater than that of the ligand substitutions in the homologous series identified above. Given the closeness of the interaction, the σ_p parameter is not necessarily the most appropriate parameter to use but pragmatically it works while parameters such as R^{33} do not, and σ^* and σ^+ cannot be adequately tested.

This direct correlation provides an exciting opportunity for greatly expanding the $E_L(L)$ database. Thus, the correlations shown in Tables 1 and 2 may now be used not only to derive $E_L(L)$ for many substituted ligands but also for a variety of exotic ligands chosen, for example, from Table I of ref. 33; ie. ligands which may be more common in organometallic chemistry. Some of these predicted $E_L(L)$ values are presented in Table 3.

It remains to be seen if ligands such as NH_2^- , which are likely to be strongly π -bonded to ruthenium, can be treated in such a simple fashion. One may also question in the future whether multiple substituents in the same ligand can be linearly treated with Eqn.(2); this does appear to be possible to the extent that it has been tested in the species discussed here. Future work will also address how the reaction parameters change with other metal ions, to see how substituent effects are transmitted to couples other than Ru^{III/II}, and whether multi-parameter fits⁴² may offer advantages. One may also expect that careful analysis of Hammett or Taft parameters giving good correlations with $E_L(L)$, compared with those that do not, will provide additional information about the factors determining such relationships.

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Table 1. Correlation parameters for $E_L(L)$ vs $\Sigma\sigma$ plots.^a

Ligand	$S' M$	$E_L(LH)$	ρ^b	R^c	sample size
benzoquinonediimines - σ_p	0.17	0.26	2.9	0.98	6
phosphines - σ_*	0.17	0.35	2.9	0.95	10
pyridines - $\Sigma\sigma^d$	0.13	0.24	2.2	0.95	17
bipyridines - $\Sigma\sigma$	0.07	0.25	1.2	0.99	16
diketones - σ^+	0.12	0.01	2.0	0.98	13
direct - σ_p^e	0.62	-0.37	10.5	0.95	20

a) Solutions to eqn. (3). See text for detail concerning parameter used. Values of σ_m and σ_p , of σ^* and of σ^+ were taken from Tables I, II and V, of ref.³³ respectively. Actual data are listed in the Appendix. b) Reaction parameter for $\text{Ru}^{III/II}L$. c) The regression coefficient. d) $\Sigma\sigma = \sigma_m + \sigma_p$ as appropriate for the species concerned. e) Solution to Eqn. 3; also see Tables 2 and 3.

Table 2. Species which act as ligands and substituents.

Species (X)	$\sigma_p(X)^a$	$E_L(X^-)^b$
OH	-0.37	-0.59
SPh	0.07	-0.53
F	0.06	-0.42
N ₃	0.08	-0.3
H	0	-0.3
NCO	0.19	-0.25
I	0.18	-0.24
Cl	0.23	-0.24
Br	0.23	-0.22
OCOCF ₃	0.46	-0.15
NO ₃	0.7	-0.11
NCS	0.52	-0.06
NO ₂	0.78	0.02
CN	0.66	0.02
NH ₃ ⁺	0.6	0.07
S(Me) ₂ ⁺	0.9	0.31
P(Me) ₃ ⁺	0.73	0.33
P(Et) ₃ ⁺	0.98	0.34
PMePh ₂ ⁺	1.18	0.37
N ₂ ⁺	1.91	0.68

a) Values obtained from ref.³³. b) Values obtained from ref.¹

Table 3. Predicted $E_L(L)$ Values

Species (X)	$\sigma_p(X)^a$	$E_L(X^-)^b$
NH ₂	-0.66	-0.78
NHPh	-0.56	-0.71
NMe ₃ ⁺	0.82	0.13
HS	0.15	-0.28
Me	-0.17	-0.47
CF ₃	0.54	-0.04
Acetate	-0.16	-0.47
SiMe ₃	-0.07	-0.41
CMe ₃	-0.2	-0.49
Ph	-0.01	-0.38
C ₆ F ₅	0.27	-0.20
Si(NMe ₂) ₃	-0.04	-0.39

a) Values obtained from ref.³³. b) Values obtained using Eqn. 3 (see Table 1, bottom entry).

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37. Consider a series of complexes having the general form, $M(L')_n^{(LH)}$ (I) and $M(L')_n^{(LX)}$ (II), where L' represents spectator ligands which may be of one or more types, then the half-cell oxidation potentials of these species, referenced to NHE, $E_o(I)$ and $E_o(II)$ may be written

$$[M(L')_n^{(LH)}]^n + e^- \rightleftharpoons [M(L')_n^{(LH)}]^{n-1} \quad K_{eq}(LH)$$

$$\text{and } E_o(I) = \sum E_L(L') + E_L(LH) = (RT/nF) \ln K_{eq}(LH)$$

$$[M(L')_n^{(LX)}]^m + e^- \rightleftharpoons [M(L')_n^{(LX)}]^{m-1} \quad K_{eq}(LX)$$

$$\text{and } E_o(II) = \sum E_L(L') + E_L(LX) = (RT/nF) \ln K_{eq}(LX)$$

Then,

$$E_o(LX) - E_o(LH) = E_L(LX) - E_L(LH) = (RT/nF)(\ln K_{eq}(LX) - \ln K_{eq}(LH))$$

$$E_L(LX) - E_L(LH) = 2.303(RT/nF)\log[K_{eq}(LX)/K_{eq}(LH)]$$

But,

$$\log[K_{eq}(LX)/K_{eq}(LH)] = \rho\sigma$$

Therefore,

$$E_L(LX) = 2.303(RT/nF)\rho\sigma + E_L(LH)$$

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Figures

Figure 1. A plot of the $E_L(L)$ parameter versus the Hammett σ_p parameter for substituents capable of acting directly as ligands (Data in Table 2)

Appendix; Data used to determine the regression statistics in Table 1.

Benzoquinonediimines, $E_L(L)$, $\Sigma\sigma = \Sigma\sigma_p$ (Electrochemical data, and hence $E_L(L)$ values from ref.⁴¹);
 4-NO₂BQDI, 0.38, 0.78; 4,5-Cl₂BQDI, 0.33, 0.46; BQDI, 0.28, 0; 4,5-(CH₃)BQDI, 0.25, -0.34;
 4,5-(OME)BQDI, 0.16, -0.54; 4,5-(NH₂)BQDI, 0.01, -1.32.

Phosphines, $E_L(L)$, Taft σ^* ($E_L(L)$ values from ref.¹); Me₃P, 0.33, -0.15; Me₂HP, 0.34, -0.1; Me₂PhP,
 0.34, 0; Pr₃P, 0.34, -0.15; Et₃P, 0.34, -0.15; MePh₂P, 0.37, 0.15; Tolyl₃P, 0.37, 0.15; Ph₃P, 0.39,
 0.3; (PhO)₃P, 0.58, 1.14; (MeO)₃P, 0.42, 0.69.

Pyridines, $E_L(L)$, $\Sigma\sigma = \sigma_m + \sigma_p$ ($E_L(L)$ values from ref.¹); 4-ViPy, 0.2, -0.04; 3,5-Me₂Py, 0.21, -0.14;
 4-PhPy, 0.23, -0.01; 4-MePy, 0.23, -0.17; 4-StPy, 0.23, -0.07; 4-t-BuPy, 0.23, -0.2; Py, 0.25, 0;
 3-CONH₂Py, 0.26, 0.28; 4-ClPy, 0.26, 0.23; 4-CONH₂Py, 0.28, 0.36; 3-IPy, 0.29, 0.35;
 4-COOHPy, 0.29, 0.45; 4-AcPy, 0.3, 0.5; 4-(CHO)Py, 0.31, 0.42; 4-CNPy, 0.32, 0.66; 4-CF₃Py,
 0.32, 0.54; 3,5-Cl₂Py, 0.33, 0.74.

Bipyridines, $E_L(L)$, $\Sigma\sigma = \sigma_m + \sigma_p$ (Electrochemical data, and hence $E_L(L)$ values from refs.^{1,43,44});
 4,4'-(NEt₂)₂bpy, 0.15, -1.44; 4,4'-(Me)₂bpy, 0.23, -0.34; 4,4'-(CH=CHPh)₂bpy, 0.24, -0.14;
 5,5'-(Me)₂bpy, 0.24, -0.14; 4,4'-(Ph)₂bpy, 0.25, -0.02; bpy, 0.26, 0; 4-Clbpy, 0.27, 0.23; 4-Brbpy,
 0.27, 0.23; 4,4-Cl₂bpy, 0.29, 0.46; 4,4-Br₂bpy, 0.29, 0.46; 4,4-(CO₂Et)₂bpy, 0.31, 0.9;
 4-Me,4'vinyl-bpy, 0.23, -0.21; 4-nitrobpy, 0.30, 0.78; 4,4-(CO₂Ph)₂bpy, 0.31, 0.88;
 5,5-(CO₂Et)₂bpy, 0.32, 0.88; 4,5,4,5-Me₄bpy, 0.22, -0.48.

Electrochemical data for the species 4,4'-(OEt)₂bpy, 4,4'-(NHCOMe)₂bpy, 4,4'-(OPh)₂bpy, and
 5,5'-(NHCOMe)₂bpy, from ref.⁴³ are excluded since they fit the correlation poorly; either the
 electrochemical or the Hammett data is suspect.

Diketones, E_L^+ , σ^+ (Electrochemical data, and hence $E_L(L)$ values from refs.^{1,21,22}); (listed as derivatives of RCOCR'COR") CF₃,H,Ph, 0.05, 0.43; CF₃,H,CH₃, 0.03, 0.30; CF₃,H,CF₃, 0.17, 1.22; Ph,H,Ph, -0.04, -0.36; Ph,H,Me, -0.06, -0.49; Me,H,Me, -0.08, -0.62; Me,Br,Me, -0.03, -0.47; Me,Cl,Me, -0.03, -0.51; Me,I,Me, -0.03, -0.48; Me,Me,Me, -0.11, -0.93; Me,Ph,Me, -0.09, -0.80; CF₃,H,3-thienyl, 0.05, 0.23; CF₃,H,tBu, 0.02, 0.35.

